

The Collinear Magnetic Phases of the Geometrically-Frustrated Antiferromagnet CuFeO_2 : The Importance of Stacking

R.S. Fishman,¹ F. Ye,² J.A. Fernandez-Baca,^{2,3} J.T. Haraldsen,¹ and T. Kimura⁴

¹*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

²*Neutron Scattering Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

³*Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37831, USA and*

⁴*Division of Materials Physics, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, 560-8531, Japan*

The correct stacking of hexagonal layers is used to obtain accurate estimates for the exchange and anisotropy parameters of the geometrically-frustrated antiferromagnet CuFeO_2 . Those parameters are highly constrained by the stability of a collinear metamagnetic phase between fields of 13.5 and 20 T. Constrained fits of the spin-wave frequencies of the collinear $\uparrow\uparrow\downarrow\downarrow$ phase below 7 T are used to identify the magnetic unit cell of the metamagnetic $\uparrow\uparrow\downarrow\downarrow$ phase, which contains two hexagonal layers and 10 Fe^{3+} spins.

PACS numbers: 75.30.Ds, 75.50.Ee, 61.05.fg

Because of their rich magnetic phase diagrams, geometrically-frustrated antiferromagnets have long occupied an important place in condensed-matter physics [1]. The antiferromagnetic interactions between the Fe^{3+} spins of CuFeO_2 are geometrically frustrated within each hexagonal plane since no spin configuration can simultaneously minimize the coupling energies of all three neighbors around an equilateral triangle. Unlike for many geometrically-frustrated antiferromagnets, quantum fluctuations about the magnetic ground states of CuFeO_2 can be safely neglected due to the large $S = 5/2$ spins. Whereas geometric frustration often leads to magnetic phases with non-collinear spins and complex unit cells, magnetic anisotropy perpendicular to the hexagonal planes in CuFeO_2 produces two different collinear magnetic phases. The $\uparrow\uparrow\downarrow\downarrow$ phase [2, 3] sketched in Fig.1(a) is stable up to the field $B_{c1} \approx 7$ T. Between $B_{c2} \approx 13.5$ T and $B_{c3} \approx 20$ T, another collinear phase with a net moment of $1 \mu_B$ per Fe^{3+} ion [4, 5] has been assumed to resemble the $\uparrow\uparrow\downarrow\downarrow$ phase shown in Fig.2 for type B stacking, with 5 Fe^{3+} spins per unit cell. Incommensurate and non-collinear phases were identified between B_{c1} and B_{c2} and above B_{c3} [4, 5].

Previous efforts to understand the collinear magnetic phases [3, 4, 6] and to estimate the exchange and anisotropy parameters [7] of CuFeO_2 made the simplifying assumption that the hexagonal layers were stacked sequentially on top of each other. We now demonstrate that an accurate determination of the Heisenberg parameters must employ the correct stacking of the hexagonal layers. We also show that the stability of a metamagnetic phase between B_{c2} and B_{c3} [4, 5] strongly constrains those parameters. Whereas earlier work [7] assuming a sequential stacking was unable to explain the observed spin-wave (SW) frequencies of the zero-field twins, realistic magnetic stackings are now used to explain all features of the low-field collinear phase and to identify the magnetic unit cell of the high-field collinear phase in CuFeO_2 .

The observation of collinear magnetic phases that are

fully polarized along the $\pm \mathbf{z}$ directions at low temperatures led to the assumption [3, 6] that the Fe^{3+} spins were “Ising-like.” However, measurements of the zero-field SW frequencies [7, 8] plotted in Fig.1(b) reveal SW gaps of only about 0.9 meV at wavevectors $(H, H, L = 3/2)$ with $H = 0.21$ and 0.29 , on either side of the ordering wavevector $\mathbf{Q} = (1/4, 1/4, 3/2)$. If the spins were truly “Ising-like,” then the SW frequencies would be much higher and they would not exhibit a significant dispersion along the $(0, 0, L)$ direction [7, 9] perpendicular to the hexagonal planes. With little change in wavevectors, the SW gaps are reduced either by an applied field along the \mathbf{z} axis or by the substitution of nonmagnetic Al^{3+} ions for Fe^{3+} . Above the field B_{c1} [4, 5] or an Al concentration of about 1.6% [8], the SW gaps vanish, the magnetic ground state becomes non-collinear, and the crystals display multiferroic behavior [10, 11, 12].

Assuming that the hexagonal planes stack sequentially, we recently fit [7] the SW frequencies of pure CuFeO_2 to the predictions of the Heisenberg model

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - D \sum_i S_{iz}^2 - 2\mu_B B \sum_i S_{iz}, \quad (1)$$

which includes single-ion anisotropy D and a magnetic field B . For “Ising-like” spins, D would be much greater than the exchange parameters J_{ij} . In a further simplification, we ignored the very small ($< 0.4\%$) distortion of the hexagonal plane [5, 13] below the Néel temperature. While this distortion breaks the symmetry between the $(H, H, 0)$, $(H, 0, 0)$ and $(0, H, 0)$ directions, thereby favoring the $\uparrow\uparrow\downarrow\downarrow$ phase with wavevector \mathbf{Q} over its twins, it can produce only a very small change in the exchange parameters and hence in the SW frequencies. Despite these simplifications, the SW dispersions evaluated along the $(H, H, 3/2)$ and $(0, 0, L)$ axis agree quite well with inelastic neutron-scattering measurements [7]. However, we were unable to fit the frequency of the two twins with wavevectors rotated $\pm\pi/3$ away from \mathbf{Q} in the $(H, K, 3/2)$ plane. Without attempting to fit the

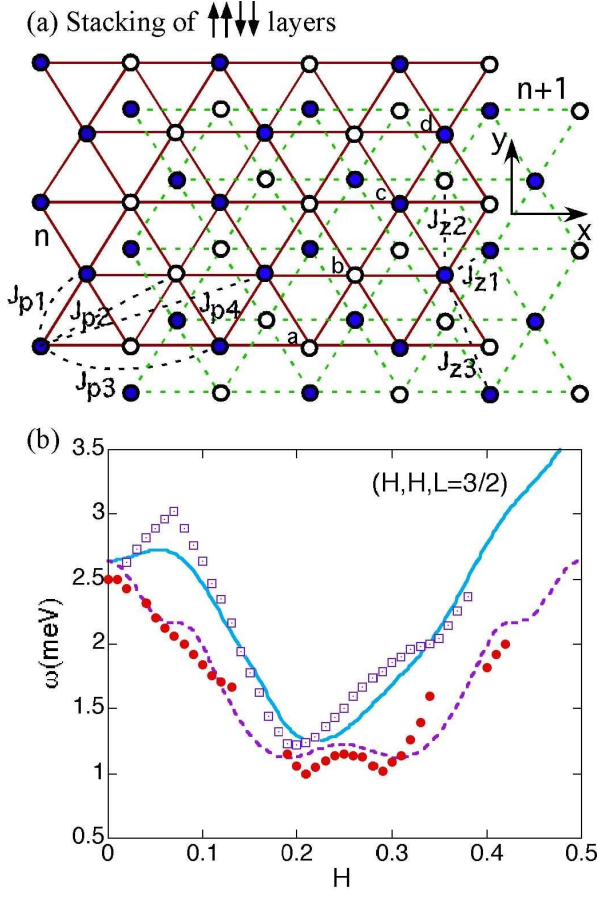


FIG. 1: (a) The low-field spin configuration (up spins are empty and down spins are filled circles) in each hexagonal plane, with the four inequivalent spins a , b , c , and d . Both the n (solid) and $n+1$ (dashed) layer are shown with the exchange parameters indicated. (b) The fit of the SW frequencies along the $(H, H, L=3/2)$ axis using the exchange and anisotropy parameters given in line *iii* of Table I. Open squares give the frequencies of the twins and solid circles the frequencies of the main SW branch with ordering wavevector at $H = 1/4$.

twins, we obtained the exchange and anisotropy parameters given in line *i* of Table I, where J_{pm} or J_{zm} are the m th nearest-neighbor exchange parameters within each hexagonal plane or between adjacent planes.

To better understand the metamagnetic phase between B_{c2} and B_{c3} , we have recalculated the SW frequencies of the $\uparrow\uparrow\downarrow\downarrow$ phase below B_{c1} using the realistic magnetic stacking of the hexagonal layers shown in Fig.1(a). All other stackings of the $\uparrow\uparrow\downarrow\downarrow$ layers have higher coupling energies. Because spins a , b , c , or d experience the same local environment on every layer, the magnetic unit cell still contains only 4 sublattices (SLs). The first few exchange pathways J_{pm} and J_{zm} are indicated in Fig.1(a).

The SW frequencies are evaluated using a Holstein-Primakoff (HP) $1/S$ expansion about the classical limit. On the spin-up a and b sites, we replace $S_{iz} = S - \alpha_i^\dagger \alpha_i$, $S_i^+ = S_{ix} + iS_{iy} = \sqrt{2S}\alpha_i$, and $S_i^- = S_{ix} - iS_{iy} = \sqrt{2S}\alpha_i^\dagger$

TABLE I: Heisenberg parameters of CuFeO_2 obtained from fits of the zero-field SW frequencies. Line *i* assumes sequential stacking of the hexagonal layers [7], *ii* and *iii* use the realistic stacking in Fig.1(a) while *iii* also constrains the parameters to stabilize the collinear phase between B_{c2} and B_{c3} . Exchange and anisotropy parameters are in meV; T_N^{MF} is in K.

fit	J_{p1}	J_{p2}	J_{p3}	J_{p4}	J_{z1}	J_{z2}	J_{z3}	D	T_N^{MF}
<i>i</i>	-0.46	-0.20	-0.26		-0.13	0.00		0.07	46
<i>ii</i>	-0.75	-0.17	-0.10	0.01	-0.51	-0.19	-0.06	0.14	65
<i>iii</i>	-0.23	-0.12	-0.16	0.00	-0.06	0.07	-0.05	0.22	25

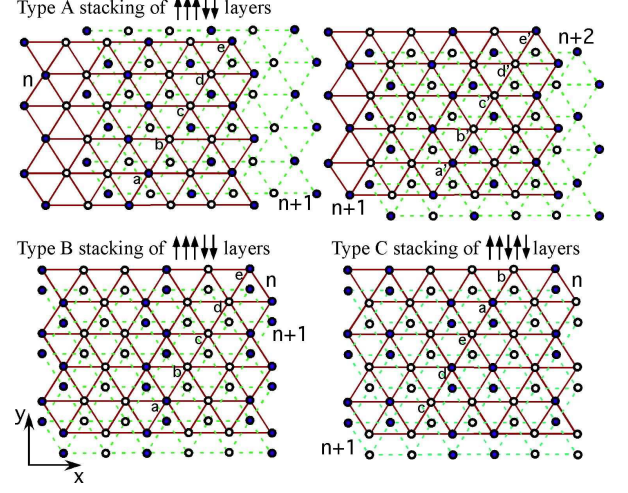


FIG. 2: Three types of magnetic stacking that satisfy the conditions for local stability of the metamagnetic phase. In type A stacking, the stacking patterns on the left and right alternate.

($\alpha_i = a_i$ or b_i). On the the spin-down c and d sites, we replace $S_{iz} = -S + \gamma_i^\dagger \gamma_i$, $S_i^+ = \sqrt{2S}\gamma_i^\dagger$, and $S_i^- = \sqrt{2S}\gamma_i$ ($\gamma_i = c_i$ or d_i). The SW frequencies $\omega_{\mathbf{k}}$ at wavevector \mathbf{k} are then obtained by solving the equations-of-motion for the vectors $\mathbf{v}_{\mathbf{k}} = (a_{\mathbf{k}}, b_{\mathbf{k}}, c_{\mathbf{k}}^\dagger, d_{\mathbf{k}}^\dagger)$ and $\mathbf{v}_{\mathbf{k}}^\dagger$. The equation-of-motion for $\mathbf{v}_{\mathbf{k}}$ may be written in terms of the 4×4 matrix $\underline{M}(\mathbf{k})$ as $id\mathbf{v}_{\mathbf{k}}/dt = -[H, \mathbf{v}_{\mathbf{k}}] = \underline{M}(\mathbf{k})\mathbf{v}_{\mathbf{k}}$ with SW frequencies given by the condition $\text{Det}(\underline{M}(\mathbf{k}) - \omega_{\mathbf{k}}\underline{I}) = 0$. Only positive frequencies $\omega_{\mathbf{k}} \geq 0$ are retained.

As expected for a collinear antiferromagnet and shown schematically for any wavevector in Fig.3(a), each of the SW branches is linearly split by a magnetic field. The lowest SW frequency with wavevector $(0.21, 0.21, 1.5)$ or $(0.29, 0.29, 1.5)$ will vanish at the field $0.9 \text{ meV}/2\mu_B \approx 7.7 \text{ T}$, which is slightly larger than B_{c1} . With the correct stacking of the hexagonal layers, the parameters in line *ii* of Table I are obtained by fitting the SW frequencies of the main branches along the $(H, H, 3/2)$ and $(0, 0, L)$ axis as well as the SW frequencies of the twins evaluated along $(H, H, 3/2)$.

There are several possible collinear metamagnetic phases with a net moment of $1 \mu_B$ per Fe^{3+} ion and with

elastic peaks at wavevectors $(m/5, m/5, 0)$ in the $L = 0$ basal plane [4]. Two configurations are possible in each hexagonal plane: the $\uparrow\uparrow\uparrow\downarrow\downarrow$ pattern sketched in the lower left of Fig.2 and the $\uparrow\uparrow\downarrow\uparrow\downarrow$ pattern sketched in the lower right. Depending on the stacking, the magnetic unit cell of the metamagnetic phase may contain either 5 or 10 magnetic ions. For example, type A stacking of $\uparrow\uparrow\uparrow\downarrow\downarrow$ layers in Fig.2 contains 10 SLs, while type B stacking of $\uparrow\uparrow\uparrow\downarrow\downarrow$ layers and type C stacking of $\uparrow\uparrow\downarrow\uparrow\downarrow$ layers contain 5 SLs. In type A stacking, the local environments of spin a on layer n and spin a' on layer $n + 1$ are different: a is coupled by J_{z1} to three up spins on layer $n + 1$ while a' is coupled by J_{z1} to two up spins and one down spin on layer $n + 2$. In types B and C stacking, the spins in layer $n + 1$ are obtained from those in layer n by the displacement $-\sqrt{3}\mathbf{y}/3$. For a 5 or 10 SL stacking, the matrix $\underline{M}(\mathbf{k})$ that enters the equations-of-motion for the SW frequencies is 5 or 10 dimensional and the 5 or 10 SW branches s must be solved numerically for every \mathbf{k} .

Two conditions must be satisfied for the local stability of a metamagnetic phase. First, the SW frequencies $\omega_{\mathbf{k}}^{(s)}$ must all be real. This condition is independent of the magnetic field, which only shifts the frequencies by $\pm 2\mu_B B$, and is not always satisfied because $\underline{M}(\mathbf{k})$ is not Hermitian. Second, the SW weights $W_{\mathbf{k}}^{(s)}$ that appear as coefficients of the delta functions in the spin-spin correlation function

$$S(\mathbf{k}, \omega) = \frac{1}{N} \int dt e^{-i\omega t} \sum_{i,j} e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)} \left\{ \langle S_i^+ S_j^-(t) \rangle + \langle S_i^- S_j^+(t) \rangle \right\} = \sum_s W_{\mathbf{k}}^{(s)} \delta(\omega - \omega_{\mathbf{k}}^{(s)}) \quad (2)$$

must all be positive. Those weights are most easily evaluated by expanding $S(\mathbf{k}, \omega)$ within the HP formalism and then solving the equations-of-motion for the spin Green's functions. An equivalent but much easier way to guarantee that the weights $W_{\mathbf{k}}^{(s)}$ are positive is to examine the field-dependence of the SW frequencies. For a stable 5 SL collinear phase, 3 of the 5 SW modes must linearly increase with field while 2 must linearly decrease, as shown in Fig.3(a). For a stable 10 SL collinear phase, 6 of the 10 SW modes must linearly increase and 4 must linearly decrease with field. If this condition is violated for any \mathbf{k} , then some of the weights $W_{\mathbf{k}}^{(s)}$ will be negative and the phase will be unstable.

Unfortunately, the exchange and anisotropy parameters given by lines *i* and *ii* of Table I do not satisfy both conditions for the local stability of any possible stacking of $\uparrow\uparrow\uparrow\downarrow\downarrow$ or $\uparrow\uparrow\downarrow\uparrow\downarrow$ layers between the fields B_{c2} and B_{c3} . In other words, fits to the SW frequencies of the zero-field $\uparrow\uparrow\downarrow\downarrow$ phase are inconsistent with the existence of a collinear metamagnetic phase.

This inconsistency may be eliminated by fitting the zero-field SW frequencies of the $\uparrow\uparrow\downarrow\downarrow$ phase while simultaneously constraining the exchange and anisotropy parameters to stabilize a metamagnetic phase between B_{c2} and B_{c3} . We emphasize that this constraint utilizes only

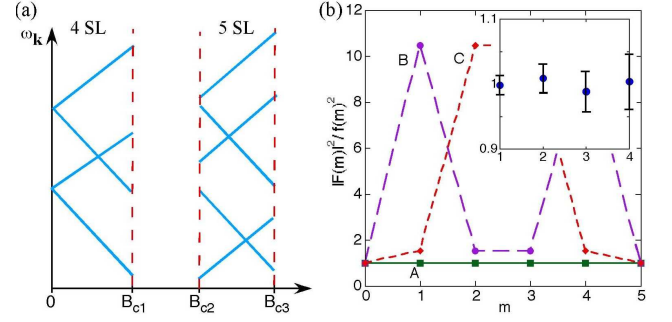


FIG. 3: (a) Schematic field dependence of the SW frequencies $\omega_{\mathbf{k}}^{(s)}$ in 4 or 5 SL phases. (b) The predicted elastic intensities $|F(m)|^2$ normalized by the Fe^{3+} form factor $f(m)^2$ versus m ($H = m/5$ along the $(H, H, 0)$ axis) for stackings A, B, and C of the metamagnetic phases. Inset are the experimental, normalized intensities versus m .

the observed stability of the metamagnetic phase over a range of magnetic fields and not the measured SW frequencies of that phase. The three phases shown in Fig.2 are the only ones that satisfy both conditions for local stability when the exchange and anisotropy parameters are obtained from constrained zero-field fits of the SW frequencies.

To determine which of these three phases is observed, we evaluate the magnetic structure factor $F(m)$ for the elastic peaks in the $L = 0$ basal plane at wavevectors $(H, H, 0)$ with $H = m/5$:

$$F^A(m) = f(m)e^{2\pi i H}, \quad (3)$$

$$F^B(m) = f(m)e^{2\pi i H} \left\{ 2i \sin 2\pi H + 2i \sin 4\pi H + 1 \right\}, \quad (4)$$

$$F^C(m) = f(m)e^{2\pi i H} \left\{ 2 \cos 2\pi H - 2i \sin 4\pi H - 1 \right\}, \quad (5)$$

where $f(m)$ is the magnetic form factor of each Fe^{3+} ion. Notice that $F(0) = f(0)$ for all three possible phases. The normalized intensities $|F(m)|^2/f(m)^2$ are plotted versus m in Fig.3(b). When the magnetic moments of 6 adjacent layers are summed, stacking A produces the pattern $0\uparrow 000$ along \mathbf{x} so that $|F^A(m)|^2/f(m)^2 = 1$ is constant. If the stacking pattern on the left or right top panel of Fig.2 were continued indefinitely rather than alternating, then the resulting phase would have no elastic peaks in the $L = 0$ basal plane. The layer sums of stackings B or C produce $\uparrow\uparrow\uparrow\downarrow\downarrow$ or $\uparrow\uparrow\downarrow\uparrow\downarrow$ patterns along \mathbf{x} , causing $|F(m)|^2/f(m)^2$ to change by a factor of 10.5 as m increases from 1 to 2.

For comparison, the experimental results [10] for the elastic intensities are plotted in the inset to Fig.3(b). The normalized intensity $|F(m)|^2/f(m)^2$ for $m = 1$ through 4 is constant to within about 1%. Therefore, only type A stacking of $\uparrow\uparrow\uparrow\downarrow\downarrow$ layers with a 10 SL unit cell is possible.

The exchange and anisotropy parameters associated with stacking A are given on line *iii* of Table I. As in our

original fits [7], $|J_{p3}| > |J_{p2}|$ but J_{p4} is negligible. Since J_{z3} is comparable to J_{z1} , even longer-ranged interactions between neighboring planes might exist. All of the interactions J_{zm} between adjacent planes are much smaller in magnitude than the interactions J_{pm} ($m < 4$) within a plane. Using these parameters, the fits of the main and twin SW branches are plotted along the $(H, H, 3/2)$ axis in Fig.1(b).

Constraining the fits of the zero-field SW frequencies to produce a stable metamagnetic phase has a substantial effect on the exchange and anisotropy parameters. For example, J_{p1} is reduced by about 70% from line *ii* to line *iii* of Table I. While a wide range of parameters can provide reasonable fits to the zero-field SW data, demanding that a metamagnetic phase is stabilized between B_{c2} and B_{c3} considerably narrows the possible range of those parameters. Also notice that the mean-field transition temperature T_N^{MF} listed in line *iii* of Table I is much closer to the measured transition temperature of 14 K [4] between partially-disordered and paramagnetic phases than the transition temperatures of the unconstrained fits in lines *i* and *ii*. Of all three fits, line *iii* produces a crystal-field environment that is most “Ising-like,” with the anisotropy D about the same size as the nearest-neighbor exchange J_{p1} . The difference between the parameters in lines *i*, *ii*, and *iii* of Table I underscores the danger of using even an extensive set of SW measurements for a single magnetic phase to fix the parameters of a Heisenberg model.

Surprisingly, the high-field collinear phase is the 10 SL

phase sketched in Fig.2 rather than the 5 SL phase that had been previously assumed [4, 5]. Because it remains locally stable up to about 34.5 T (very close to the critical field B_{c4} measured by Terada *et al.* [5]), the disappearance of the 10 SL $\uparrow\uparrow\uparrow\downarrow$ phase at B_{c3} probably occurs at a first-order transition between collinear and non-collinear phases. That appears to be the case for the $\uparrow\uparrow\downarrow$ phase, since B_{c1} is lower than the 7.7 T field where the SW gap would vanish and the $\uparrow\uparrow\downarrow$ phase would become locally unstable. The 10 SL $\uparrow\uparrow\uparrow\downarrow$ phase remains locally stable only down to B_{c2} , where the frequency of a SW mode vanishes.

Our work demonstrates that the stacking of the hexagonal planes and the stability of a metamagnetic phase play crucial roles in determining the exchange and anisotropy parameters of a frustrated antiferromagnet. By constraining the fitting parameters at zero field, we have been able to identify the magnetic unit cell of the collinear metamagnetic phase in CuFeO_2 . Constrained zero-field fits may prove to be a powerful technique for other systems as well.

We would like to acknowledge helpful conversations with Satoshi Okamoto. This research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC for the U. S. Department of Energy under Contract No. DE-AC05-00OR22725 and by the Division of Materials Science and Engineering and the Division of Scientific User Facilities of the U.S. DOE.

-
- [1] See, for example, *Frustrated Spin Systems* (World Scientific, New Jersey, 2004), edited by H.T. Diep.
 - [2] S. Mitsuda, H. Yoshizawa, N. Yaguchi, and M. Mekata, *J. Phys. Soc. Jpn.* **60**, 1885 (1991).
 - [3] M. Mekata, N. Yaguchi, T. Takagi, T. Sugino, S. Mitsuda, H. Yoshizawa, N. Hosoito, and T. Shinjo, *J. Phys. Soc. Jpn.* **12**, 4474 (1993).
 - [4] S. Mitsuda, M. Mase, T. Uno, H. Kitazawa, and H.A. Katori, *J. Phys. Chem. Sol.* **60**, 1249 (1999); S. Mitsuda, M. Mase, K. Prokes, H. Kitazawa, and H.A. Katori, *J. Phys. Soc. Jpn.* **69**, 3513 (2000).
 - [5] N. Terada, Y. Narumi, K. Katsumata, T. Yamamoto, U. Staub, K. Kindo, M. Hagiwara, Y. Tanaka, A. Kikkawa, H. Toyokawa, T. Fukui, R. Kanmuri, T. Ishikawa, and H. Kitamura, *Phys. Rev. B* **74**, 180404(R) (2006); N. Terada, Y. Narumi, Y. Sawai, K. Katsumata, U. Staub, Y. Tanaka, A. Kikkawa, T. Fukui, K. Kindo, T. Yamamoto, R. Kanmuri, M. Hagiwara, H. Toyokawa, T. Ishikawa, and H. Kitamura, *Phys. Rev. B* **75**, 224411 (2007).
 - [6] T. Takagi and M. Mekata, *J. Phys. Soc. Jpn.* **64**, 4609 (1995).
 - [7] F. Ye, J.A. Fernandez-Baca, R.S. Fishman, Y. Ren, H.J. Kang, Y. Qiu, and T. Kimura, *Phys. Rev. Lett.* **99**, 157201 (2007); R.S. Fishman, *J. Appl. Phys.* **103**, 07B109 (2008).
 - [8] N. Terada, S. Mitsuda, Y. Oohara, H. Yoshizawa, and H. Takei, *J. Magn. Magn. Mat.* **272-276**, e997 (2004); N. Terada, S. Mitsuda, K. Prokes, O. Suzuki, H. Kitazawa, and H.A. Katori, *Phys. Rev. B* **70**, 174412 (2004); N. Terada, S. Mitsuda, T. Fujii, and D. Petitgrand, *J. Phys.: Cond. Mat.* **19**, 145241 (2007).
 - [9] O.A. Petrenko, M.R. Lees, G. Balakrishnan, S. de Brion, and G. Chouteau, *J. Phys.: Cond. Mat.* **17**, 2741 (2005).
 - [10] S. Kanetsuki, S. Mitsuda, T. Nakajima, D. Anazawa, H.A. Katori, and K. Prokes, *J. Phys.: Cond. Mat.* **19**, 145244 (2007).
 - [11] T. Kimura, J.C. Lashley, and A.P. Ramirez, *Phys. Rev. B* **73**, 220401(R) (2006).
 - [12] S. Seki, Y. Yamasaki, Y. Shiomi, S. Iguchi, Y. Onose, and Y. Tokura, *Phys. Rev. B* **75**, 100403(R) (2007).
 - [13] F. Ye, Y. Ren, Q. Huang, J.A. Fernandez-Baca, P. Dai, J.W. Lynn, and T. Kimura, *Phys. Rev. B* **73**, 220404(R) (2006).